V.N.8 Computer Simulation of Proton Transport in Fuel Cell Membranes

Gregory A. Voth
University of Utah
Department of Chemistry
Salt Lake City, UT 84112-0850
Phone: (801) 581-7272; Fax: (801) 581-4353
E-mail: voth@chem.utah.edu

DOE Program Officer: William Millman
Phone: (301) 903-5805
E-mail: william.millman@science.doe.gov

Objectives

To develop and apply novel atomistic and multiscale computer simulation methods to study and predict proton solvation and transport behavior in polymer electrolyte membranes for fuel cell applications. These simulations will utilized to better understand the behavior of existing membranes such as Nafion™, as well as to predict the properties of new membranes being synthesized by experimentalists.

Technical Barriers

The physical and chemical environment of polymer electrolyte membranes is an extremely challenging one to study by atomistic molecular dynamics computer simulation methods. The concentration of excess protons is very high (as high as 10 M), the protons may shuttle through intervening water molecules via Grotthuss shuttling, and the underlying polymeric material is highly heterogeneous. The timescales of motion that influence the proton transport behavior also bridge several orders of magnitude.

Abstract, Progress Report and Future Directions

The solvation and transport of excess protons in polymer electrolyte membranes (PEM) such as Nafion™ has been computationally studied using the multi-state empirical valence bond (MS-EVB) method, combined with large scale molecular dynamics (MD) computer simulation. The MS-EVB method allows for the treatment of explicit (Grotthuss) proton shuttling and delocalization, which, in turn, strongly influences the properties of excess protons in various aqueous and otherwise complex environments. A significant extension of the MS-EVB methodology to treat highly acidic (low pH) environments such as the hydrophilic domains of PEM has been developed.[1] This extension, called self-consistent iterative MS-EVB (SCI-MS-EVB) has allowed our group, for the first time,[2] to simulate the explicit solvation and transport of excess protons in the PEM Nafion™. Results on proton solvation and transport in such environments will be presented, revealing the significant role of Grotthuss shuttling in the acidic group proton dissociation process, as well as on the subsequent excess proton solvation structures and transport properties. The proton delocalization arising from the Grotthuss shuttling causes the absence of any appreciable contact ion pair species between the dissociated hydronium species and the sulfonate anion groups tethered to the polymer backbone. A surprising result has additionally been found that Grotthuss shuttling (hopping transport) and Einstein diffusion (vehicular transport) have a large anti-correlation, so that their overall combined contribution to the proton diffusion constant is not simply additive. The Grotthuss hopping process instead serves to impede proton diffusion to a certain degree, a counter-intuitive result at odds with most assumptions regarding the hopping contribution to PEM proton transport. Evidence is also seen to implicate the correlation of the protonated water clusters with the motions of the polymer backbone on a 500 ps timescale, which is two order of magnitude slower than the characteristic hopping time of protons between water molecules via the Grotthuss shuttling process. Results on all of the above phenomena as a function of PEM hydration will also be presented. Perspectives on the future design of future PEMs with enhanced proton transport properties will be provided based on these simulations.

References

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2. M. K. Petersen and G. A. Voth, "Characterization of the Solvation and Transport of the Hydrated Proton in the Perfluorosulfonic Acid Membrane Nafion™," J. Phys. Chem. B 110, 18594 (2006).

Publications (Including Patents) Acknowledging the Grant or Contract

1. M. K. Petersen and G. A. Voth, "Characterization of the Solvation and Transport of the Hydrated Proton in the Perfluorosulfonic Acid Membrane Nafion™," J. Phys. Chem. B **110**, 18594-18600 (2006).